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54 **Surfactant agglomerate particle.**

57 There is provided a particulate agglomerate detergent component comprising a solid salt, and a binder, wherein said binder is applied as a fluid and comprises

- a) at least 20% by weight of alkali metal silicate; and
- b) at least 30% by weight of anionic surfactant

such that the weight ratio of said anionic surfactant to said alkali metal silicate is from 1:3 to 3:1. There is also provided a process for making particulate agglomerate detergent components.

EP 0 651 050 A1

The present invention relates to a particulate agglomerate detergent component comprising a salt and a binder, where said binder is applied in fluid form and comprises anionic surfactant and alkali metal silicate. Another aspect of the invention relates to a process for making particulate agglomerate detergent components.

5 In recent years there has been a trend towards making granular detergents having a higher bulk density than before. Various techniques of making dense granular detergents, and of processing low density granular detergents in such a way that the bulk density is increased, have been described. One example of a suitable technique for making dense granular detergents is known as "agglomeration". This term herein describes any process in which small particles of the components are processed in such a way that they
10 are built-up (or "agglomerated") to form suitable granular components.

The agglomerate particle should show acceptable physical characteristics, such as acceptable hardness and flow properties. It should be possible to make the agglomerate via a manufacturing process which is both efficient and versatile.

US 5 080 848, published on 14th January, 1992 describes a process for making surfactant granules
15 typically having an anionic surfactant activity of 50% to 75% (see examples 1 to 8). The process involves chilling and granulating a viscous high active surfactant paste. The granulation may be performed with the aid of some detergency builders (see examples 3 and 4), but the emphasis is on reducing the temperature in order to initiate granulation.

EP 0 508 543, published on 14th October, 1992 discloses methods of chemically conditioning high
20 active surfactant pastes in order to achieve high active detergent granules. Silicates are generally disclosed as useful conditioning agents. Conditioning of a paste may be achieved by, for example, increasing paste viscosity and/or drying.

When incorporated into agglomerate particles, certain anionic surfactants, particularly the alkyl ethoxysulfate surfactants, can tend to make the particles sticky, causing poor flow characteristics, and caking of
25 the product. The inclusion of these anionic surfactants can also tend to result in particles which are soft and insufficiently robust to break up of the particle.

It has now been surprisingly found that detergent particles having good hardness and flow properties can be made by agglomerating salts using a fluid binder containing a high active solution of anionic surfactant and silicate, at specific ratios of silicate to anionic surfactant.

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Summary of the invention

There is provided a particulate agglomerate detergent component comprising a solid salt, and a binder, wherein said binder is applied as a fluid and comprises

35 a) at least 20% by weight of alkali metal silicate; and

b) at least 30% by weight of anionic surfactant

such that the weight ratio of said anionic surfactant to said alkali metal silicate is from 1:3 to 3:1.

Detailed Description of the invention

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The particulate agglomerate detergent component comprises a solid salt and a binder which is applied to said solid salt as a fluid. By particulate agglomerate component is meant herein a particle made by an agglomeration process.

The particulate agglomerate component preferably has a particle size of from 150µm to 1400µm, more
45 preferably from 250µm to 1000µm.

The first essential element of the particulate agglomerate detergent component of the invention is a solid salt, which is preferably in particulate form.

The salt can be selected from essentially any of the salts commonly employed in detergent compositions. The salt may be water-soluble or water-insoluble, but where the proposed application is to machine
50 dishwashing compositions, where insoluble salt deposition on articles in the wash is a problem, it is most preferred that the salt is water-soluble. While the salt may be inert, it preferably also functions as detergency builder material in the wash solution. The salt assists in providing the desired density and bulk to the detergent granules herein.

Suitable solid salts preferably have a particle size of from 10µm to 300µm, more preferably from 20µm
55 to 100µm.

Examples of water-soluble inorganic salts include the alkali metal, ammonium or substituted ammonium chlorides, fluorides and sulfates. The alkali metal, and especially sodium, salts of the above are preferred. Sodium sulfate is typically used in detergent granules and is a particularly preferred salt. Alkali metal

silicate is another useful inorganic salt, herein.

Other useful salts include the compounds commonly known as detergent builder materials. Builders are generally selected from the alkali metal, ammonium or substituted ammonium phosphates, polyphosphates, phosphonates, polyphosphonates, carbonates, bicarbonates, sesquicarbonates, citrates, borates, crystalline
5 layered silicates, aluminosilicates (zeolites), and polyhydroxysulfonates. Preferred are the alkali metal, especially sodium, salts of the above.

Specific examples of inorganic phosphate builders are sodium and potassium tripolyphosphate, pyrophosphate, polymeric metaphosphate having a degree of polymerization of from about 6 to 21, and orthophosphate.

10 In a particularly preferred execution the solid salt comprises a mixture of sodium silicate of $\text{SiO}_2:\text{Na}_2\text{O}$ ratio of from 2.2:1.0 to 1.8:1.0 preferably, 2.0:1.0, and sodium sulphate, at a weight ratio of sodium silicate to sodium sulfate of from 2:1 to 1:1, preferably 3:2.

The second essential component of the particulate agglomerate detergent component of the invention is a binder, wherein said binder is applied as a fluid and where the term 'fluid' includes pastes and liquids, but
15 preferably means liquids. The fluid should be of a viscosity which allows for its pumping under the process conditions generally employed in the processing of detergent paste and liquid compositions. Process conditions involving pumping under pressure, and at elevated temperatures are envisaged.

The binder acts to bind the solid salt and any other components of the agglomerate particle so as to give a particulate component which is desirably non-friable and non-sticky, and hence has acceptable bulk
20 flow properties.

The particles should also be structured such that when introduced into a wash solution, under typical wash conditions, rapid disintegration of the particle, and hence release of the detergent components thereof, occurs. Typical wash solution concentrations experienced, for example, in laundry and machine dishwashing methods are in the region of 0.1% to 2% product concentration. Typical wash temperatures will be in
25 the range of 20°C to 95°C.

The binder comprises at least 20% by weight preferably at least 30% by weight, of alkali metal silicate wherein said alkali metal silicate is most preferably incorporated into said binder as a high active solution, comprising at least 60%, preferably at least 70% by weight of the solution of alkali metal silicate. The alkali metal silicate has a molar ratio of $\text{SiO}_2:\text{Na}_2\text{O}$ of from 1.0 to 2.8, preferably from 1.6 to 2.4, most preferably
30 2.0.

The binder also comprises at least 30% preferably at least 40%, by weight of anionic surfactant.

In the binder, the weight ratio of the alkali metal silicate to anionic surfactant is from 1:3 to 3:1, preferably from 1:2 to 2:1, most preferably 1:1.5 to 1.5:1.

In a particularly preferred execution the binder additionally incorporates from 1% to 20% by weight of
35 particulate salt selected from the group consisting of alkali metal silicate, carbonate and sulphate salts, and any mixtures thereof, wherein the average particle size of the particulate salt is from 10 to 300µm, more preferably from 20 to 100µm.

Anionic surfactant

40 The anionic surfactant may be essentially any anionic surfactant. Anionic surfactants useful herein are listed in U.S. Pat. No. 3,664,961, Norris, issued May 23, 1972, and in U.S. Pat. No. 3,919,678, Laughlin et al., issued Dec. 30, 1975 at Column 23, line 58 through Column 29, line 23.

Suitable anionic surfactants include the salts (including, for example, sodium, potassium, ammonium, and substituted ammonium salts such as mono-, di- and triethanolamine salts) of the organic sulfates,
45 organic sulfonates, alkyl ethoxy carboxylates, sarcosinates, alkyl phosphates, isethionates such as the acyl isethionates, N-acyl taurates, fatty acid amides of methyl tauride, soaps, alkyl succinates and sulfosuccinates, monoesters of sulfosuccinate (especially saturated and unsaturated $\text{C}_{12}\text{-C}_{18}$ monoesters) diesters of sulfosuccinate (especially saturated and unsaturated $\text{C}_6\text{-C}_{14}$ diesters), N-acyl sarcosinates, and fatty
50 acids esterified with isethionic acid and neutralized with sodium hydroxide. Resin acids and hydrogenated resin acids are also suitable, such as rosin, hydrogenated rosin, and resin acids and hydrogenated resin acids present in or derived from tallow oil. Further examples are given in "Surface Active Agents and Detergents" (Vol. I and II by Schwartz, Perry and Berch).

Anionic sulfate, sulfonate and alkyl ethoxy carboxylate surfactants are particularly preferred for use
55 herein.

Anionic sulfate surfactant

The anionic sulfate surfactant may be any organic sulfate surfactant. It is preferably selected from the group consisting of C₆-C₂₀ linear or branched chain alkyl sulfate which has been ethoxylated with from about 0.5 to about 20 moles of ethylene oxide per molecule, C₉-C₁₇ acyl-N-(C₁-C₄ alkyl) glucamine sulfated, -N-(C₂-C₄ hydroxyalkyl) glucamine sulfate, and mixtures thereof. More preferably, the anionic sulfate surfactant is a C₆-C₁₈ alkyl sulfate which has been ethoxylated with from about 0.5 to about 20, preferably from about 0.5 to about 5, moles of ethylene oxide per molecule.

Preferred alkyl ethoxy sulfate surfactants comprise a primary alkyl ethoxy sulfate derived from the condensation product of a C₆-C₁₈ alcohol with an average of from about 0.5 to about 20, preferably from about 0.5 to about 5, ethylene oxide groups. The C₆-C₁₈ alcohol itself is preferable commercially available. C₁₂-C₁₅ alkyl sulfate which has been ethoxylated with from about 1 to about 5 moles of ethylene oxide per molecule is preferred alkyl ethoxy sulfate surfactant. Highly branched C₁₀-C₁₈ alkyl ethoxy sulfates, with a degree of ethoxylation of from 5 to 20, in combination with linear methyl branched C₆-C₁₀ alkyl ethoxy sulfates with a degree of ethoxylation of from 5 to 20 are also preferred.

Where the compositions of the invention are formulated to have a pH of between 6 to 9.5, preferably between 7.5 to 9, wherein the pH is defined herein to be the pH of a 1% solution of the composition measured at 20°C, surprisingly robust soil removal, particularly proteolytic soil removal, is obtained when C₁₀-C₁₈ alkyl ethoxysulfate surfactant, with an average degree of ethoxylation of from 0.5 to 5 is incorporated into the composition in combination with a proteolytic enzyme, such as neutral or alkaline proteases at a level of active enzyme of from 0.005% to 2%. Preferred alkyl ethoxysulfate surfactant for inclusion in such compositions with a pH of between 6 to 9.5 are the C₁₂-C₁₅ alkyl ethoxysulfate surfactants with an average degree of ethoxylation of from 1 to 5, preferably 2 to 4, most preferably 3.

Conventional base-catalyzed ethoxylation processes to produce an average degree of ethoxylation of 12 result in a distribution of individual ethoxylates ranging from 1 to 15 ethoxy groups per mole of alcohol, so that the desired average can be obtained in a variety of ways. Blends can be made of material having different degrees of ethoxylation and/or different ethoxylate distributions arising from the specific ethoxylation techniques employed and subsequent processing steps such as distillation.

Anionic sulfate surfactants include the C₅-C₁₇ acyl-N-(C₁-C₄ alkyl) and -N-(C₁-C₂ hydroxyalkyl) glucamine sulfates, preferably those in which the C₅-C₁₇ acyl group is derived from coconut or palm kernel oil. These materials can be prepared by the method disclosed in U.S. Patent 2,717,894, Schwartz, issued September 13, 1955.

Other anionic sulfate surfactants include the fatty oleyl glycerol sulfates, alkyl phenol ethylene oxide ether sulfates, and the sulfates of alkylpolysaccharides such as the sulfates of alkylpolyglucoside (the nonionic nonsulfated compounds being described herein).

The counterion for the anionic sulfate surfactant component is preferably selected from calcium, sodium, potassium, magnesium, ammonium, or alkanol-ammonium, and mixtures thereof, more preferably sodium or potassium, or mixtures thereof.

Anionic sulfonate surfactant

Anionic sulfonate surfactants suitable for use herein include essentially any sulfonate surfactants including, for example, the salts (eg : alkali metal salts) of C₅-C₂₀ linear alkylbenzene sulfonates, C₅-C₂₂ primary or secondary alkane sulfonates, C₆-C₂₄ olefin sulfonates, sulfonated polycarboxylic acids, alkyl glycerol sulfonates, alkyl ester sulfonates, fatty acyl glycerol sulfonates, fatty oleyl glycerol sulfonates, paraffin sulfonates, and any mixtures thereof. Certain sulfonate surfactants may form precipitates with hardness ions making them less preferred for use herein.

Anionic alkyl ethoxy carboxylate surfactant

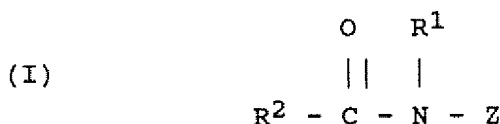
Alkyl ethoxy carboxylates suitable for use herein include those with the formula RO(CH₂CH₂O)_xCH₂COO⁻M⁺ wherein R is a C₆ to C₁₈ alkyl group, x ranges from 0 to 10, and the ethoxylate distribution is such that, on a weight basis, the amount of material where x is 0 is less than about 20 % and the amount of material where x is greater than 7, is less than about 25 %, the average x is from about 2 to 4 when the average R is C₁₃ or less, and the average x is from about 3 to 6 when the average R is greater than C₁₃, and M is a cation preferably selected from sodium, potassium, ammonium and mixtures thereof with magnesium ions. The preferred alkyl ethoxy carboxylates are those where R is a C₁₂ to C₁₈ alkyl group.

Optional surfactants

The particulate agglomerate components of the invention may also comprise optional surfactants selected from nonionic, ampholytic, zwitterionic and cationic surfactants. A typical listing of nonionic, ampholytic, and zwitterionic classes, and species of these surfactants, is given in U.S.P. 3,929,678 issued to Laughlin and Heuring on December 30, 1975. A list of suitable cationic surfactants is given in U.S.P. 4,259,217 issued to Murphy on March 31, 1981.

Nonionic polyhydroxy fatty acid amide surfactant

Polyhydroxy fatty acid amides suitable for use herein are those having the structural formula :



wherein : R¹ is H, C₁-C₄ hydrocarbyl, 2-hydroxy ethyl, 2-hydroxy propyl, or a mixture thereof, preferable C₁-C₄ alkyl, more preferably C₁ or C₂ alkyl, most preferably C₁ alkyl (i.e., methyl); and R₂ is a C₅-C₃₁ hydrocarbyl, preferably straight-chain C₅-C₁₉ alkyl or alkenyl, more preferably straight-chain C₉-C₁₇ alkyl or alkenyl, most preferably straight-chain C₁₁-C₁₇ alkyl or alkenyl, or mixture thereof; and Z is a polyhydroxyhydrocarbyl having a linear hydrocarbyl chain with at least 3 hydroxyls directly connected to the chain, or an alkoxylated derivative (preferably ethoxylated or propoxylated) thereof.

Nonionic alkylpolysaccharide surfactant

Suitable alkylpolysaccharides for use herein are disclosed in U.S. Patent 4,565,647, Llenado, issued January 21, 1986, having a hydrophobic group containing from about 6 to about 30 carbon atoms, preferably from about 10 to about 16 carbon atoms and a polysaccharide, e.g., a polyglycoside, hydrophilic group containing from about 1.3 to about 10, preferably from about 1.3 to about 3, most preferably from about 1.3 to about 2.7 saccharide units.

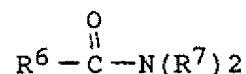
The preferred alkylpolyglycosides have the formula



wherein R² is selected from the group consisting of alkyl, alkylphenyl, hydroxyalkyl, hydroxyalkylphenyl, and mixtures thereof in which the alkyl groups contain from 10 to 18, preferably from 12 to 14, carbon atoms; n is 2 or 3, preferably from about 1.3 to about 3, most preferably from about 1.3 to about 2.7. The glycosyl is preferably derived from glucose.

Nonionic fatty acid amide surfactant

Fatty acid amide surfactants suitable for use herein are those having the formula:



wherein R⁶ is an alkyl group containing from 7 to 21, preferably from 9 to 17 carbon atoms and each R⁷ is selected from the group consisting of hydrogen, C₁-C₄ alkyl, C₁-C₄ hydroxyalkyl, and -(C₂H₄O)_xH, where x is in the range of from 1 to 3.

Ampholytic surfactant

Ampholytic surfactants can be incorporated into the detergent compositions herein. These surfactants can be broadly described as aliphatic derivatives of secondary or tertiary amines, or aliphatic derivatives of

heterocyclic secondary and tertiary amines in which the aliphatic radical can be straight chain or branched. One of the aliphatic substituents contains at least about 8 carbon atoms, typically from about 8 to about 18 carbon atoms, and at least one contains an anionic water-solubilizing group, e.g., carboxy, sulfonate, sulfate. See U.S. Patent No. 3,929,678 to Laughlin et al., issued December 30, 1975 at column 19, lines 18-35 for examples of ampholytic surfactants.

Amphoteric surfactant

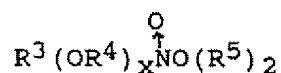
Alkyl amphocarboxylic acid amphoteric surfactant

Suitable amphoteric surfactants for use herein include the alkyl amphocarboxylic acids.

A preferred amphocarboxylic acid is produced from fatty imidazolines wherein the dicarboxylic acid functionality of the amphodicarboxylic acid is diacetic acid and/or dipropionic acid. A suitable example of an alkyl amphodicarboxylic acid for use herein in the amphoteric surfactant Miranol(TM) C2M Conc. manufactured by Miranol, Inc., Dayton, NJ.

Amine Oxide surfactant

Amine oxides useful, as amphoteric surfactants, in the present invention include those compounds having the formula :



wherein R^3 is selected from an alkyl, hydroxyalkyl, acylamidopropoyl and alkyl phenyl group, or mixtures thereof, containing from 8 to 26 carbon atoms, preferably 8 to 16 carbon atoms; R^4 is an alkylene or hydroxyalkylene group containing from 2 to 3 carbon atoms, preferably 2 carbon atoms, or mixtures thereof; x is from 0 to 5, preferably from 0 to 3; and each R^5 is an alkyl or hydroxyalkyl group containing from 1 to 3, preferably from 1 to 2 carbon atoms, or a polyethylene oxide group containing from 1 to 3, preferably 1, ethylene oxide groups. The R^5 groups can be attached to each other, e.g., through an oxygen or nitrogen atom, to form a ring structure.

These amine oxide surfactants in particular include C_{10} - C_{18} alkyl dimethyl amine oxides and C_8 - C_{18} alkoxy ethyl dihydroxyethyl amine oxides. Examples of such materials include dimethyloctylamine oxide, diethyldodecylamine oxide, bis-(2-hydroxyethyl)dodecylamine oxide, dimethyldodecylamine oxide, dipropyl-tetradecylamine oxide, methylethylhexadecylamine oxide, dodecylamidopropyl dimethylamine oxide, cetyl dimethylamine oxide, stearyl dimethylamine oxide, tallow dimethylamine oxide and tallow bis-(2-hydroxy ethyl) amine oxide. Preferred are C_{10} - C_{18} alkyl dimethylamine oxide, and C_{10} - C_{18} acylamido alkyl dimethylamine oxide.

Zwitterionic surfactant

Zwitterionic surfactants can also be incorporated into the detergent compositions hereof. These surfactants can be broadly described as derivatives of secondary and tertiary amines, derivatives of heterocyclic secondary and tertiary amines, or derivatives of quaternary ammonium, quaternary phosphonium or tertiary sulfonium compounds. See U.S. Patent No. 3,929,678 to Laughlin et al., issued December 30, 1975 at column 19, line 38 through column 22, line 48 (herein incorporated by reference) for examples of zwitterionic surfactants. Suitable amphoteric surfactants include betaine, sultaine and complex betaine surfactants.

Cationic surfactants

Cationic surfactants can also be used in the detergent compositions herein and suitable quaternary ammonium surfactants are selected from mono C_6 - C_{16} , preferably C_8 - C_{16} N-alkyl or alkenyl ammonium surfactants wherein remaining N positions are substituted by methyl, hydroxyethyl or hydroxypropyl groups.

Alkoxyated nonionic surfactant.

Alkoxyated nonionic surfactants (nonionic alkylene oxide condensate surfactants) are defined herein to include the nonionic ethoxylated alcohol surfactants, nonionic condensates of alkyl phenols, the nonionic ethoxylated/propoxylated fatty alcohols, nonionic EO/PO condensates with propylene glycol and nonionic EO condensation products with propylene oxide/ethylene diamine adducts, as described hereinafter.

Nonionic condensates of alkyl phenols

The polyethylene, polypropylene, and polybutylene oxide condensates of alkyl phenols are suitable for use herein. In general, the polyethylene oxide condensates are preferred. These compounds include the condensation products of alkyl phenols having an alkyl group containing from about 6 to about 18 carbon atoms in either a straight chain or branched chain configuration with the alkylene oxide.

Nonionic ethoxylated alcohol surfactant

The alkyl ethoxylate condensation products of aliphatic alcohols with from about 1 to about 25 moles of ethylene oxide are suitable for use herein. The alkyl chain of the aliphatic alcohol can either be straight or branched, primary or secondary, and generally contains from 6 to 22 carbon atoms. Particularly preferred are the condensation products of alcohols having an alkyl group containing from 8 to 20 carbon atoms with from about 2 to about 10 moles of ethylene oxide per mole of alcohol. Most preferred are the condensation products of alcohols having an alkyl group containing from 12 to 18 carbon atoms with from about 6 to about 10 moles of ethylene oxide per mole of alcohol.

Nonionic ethoxylated/propoxylated fatty alcohol surfactant

The ethoxylated C₆-C₁₈ fatty alcohols and C₆-C₁₈ mixed ethoxylated/propoxylated fatty alcohols are suitable surfactants for use herein, particularly where water soluble. Preferably the ethoxylated fatty alcohols are the C₁₀-C₁₈ ethoxylated fatty alcohols with a degree of ethoxylation of from 3 to 50, most preferably these are the C₁₂-C₁₈ ethoxylated fatty alcohols with a degree of ethoxylation from 3 to 40. Preferably the mixed ethoxylated/propoxylated fatty alcohols have an alkyl chain length of from 10 to 18 carbon atoms, a degree of ethoxylation of from 3 to 30 and a degree of propoxylation of from 1 to 10. A highly preferred surfactant of this type is a C13-C15 mixed ethoxylated/propoxylated fatty alcohol with an average degree of ethoxylation of 3.8, and an average degree of propoxylation of 4.5, sold under the tradename Plurafac LF404 by BASF GmbH.

Nonionic EO/PO condensates with propylene glycol

The condensation products of ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol are suitable for use herein. The hydrophobic portion of these compounds preferably has a molecular weight of from about 1500 to about 1800 and exhibits water insolubility. The addition of polyoxyethylene moieties of this hydrophobic portion tends to increase the water solubility of the molecule as a whole, and the liquid character of the product is retained up to the point where the polyoxyethylene content is about 50% of the total weight of the condensation product, which corresponds to condensation with up to about 40 moles of ethylene oxide. Examples of compounds of this type include certain of the commercially-available Pluronic™ surfactants, marketed by BASF.

Nonionic EO condensation products with propylene oxide/ethylene diamine adducts

The condensation products of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylenediamine are suitable for use herein. The hydrophobic moiety of these products consists of the reaction product of ethylenediamine and excess propylene oxide, and generally has a molecular weight of from about 2500 to about 3000. This hydrophobic moiety is condensed with ethylene oxide to the extent that the condensation product contains from about 40% to about 80% by weight of polyoxyethylene and has a molecular weight of from about 5,000 to about 11,000. Examples of this type of nonionic surfactant include certain of the commercially available Tetronic™ compounds, marketed by BASF.

Organic polymers

The particulate agglomerate components of the present invention may contain organic polymers, some of which also may function as builders to improve detergency. These polymers may be introduced into the binder component of the particulate agglomerate as a high active solution of the polymer. Included among such polymers may be mentioned sodium carboxy-lower alkyl celluloses, sodium lower alkyl celluloses and sodium hydroxy-lower alkyl celluloses, such as sodium carboxymethyl cellulose, sodium methyl cellulose and sodium hydroxypropyl cellulose, polyvinyl alcohols (which often also include some polyvinyl acetate), polyacrylamides, polyacrylates, polyaspartates, polyvinylpyrrolidones and various copolymers, such as those of maleic and acrylic acids. Molecular weights for such polymers vary widely but most are within the range of 2,000 to 100,000.

Polymeric polycarboxyate builders are set forth in U.S. Patent 3,308,067, Diehl, issued March 7, 1967. Such materials include the water-soluble salts of homo-and copolymers of aliphatic carboxylic acids such as maleic acid, itaconic acid, mesaconic acid, fumaric acid, aconitic acid, citraconic acid and methylenemalononic acid.

Most preferred for use in the present invention are copolymers of maleic and acrylic acid having a molecular weight of from 2000 to 100000, carboxymethyl cellulose and mixtures thereof.

Processing

In another aspect of the invention there is provided a process for making particulate agglomerate detergent components, wherein said process is particularly preferred for making the particulate agglomerate components of the invention as hereinbefore described, said process comprising the steps of:

- (a) mixing an anionic surfactant with a high active solution of alkali metal silicate comprising at least 60% by weight, preferably at least 70% by weight of the alkali metal silicate, to form a binder, in fluid form.
- (b) agglomerating a solid salt with an effective amount of the binder to form discrete particles
- (c) drying the agglomerated particles.

The binder preferably comprises

- a) at least 20% by weight of said alkali metal silicate; and
- b) at least 30% by weight of said anionic surfactant

such that the weight ratio of the anionic surfactant to the alkali metal silicate is from 1:3 to 3:1.

The anionic surfactant may be in essentially any form, but is preferably in fluid form, most preferably in the form of a paste premix which may be prepared by any method which is known to the man skilled in the art.

The activity of any anionic surfactant paste premix is preferably at least 40% and can go up to about 95%; preferred activities are : 50-80% and 65-75%. The balance of the paste premix is primarily water but can include a processing aid such as a liquid nonionic surfactant, or an organic solvent such as an alcohol or glycol.

Particularly useful methods include sulphation and/or sulphonation or other reactions to make the desired anionic surfactants e.g. in a falling film sulphonating reactors, digestion tanks, esterification reactors, etc. It is particularly convenient to neutralise the acid precursors of anionic surfactants in a continuous neutralisation loop. In such a piece of equipment the acid precursor is fed into a loop together with a neutralising agent such as aqueous sodium hydroxide. The components are intimately mixed to promote neutralisation and then fed through a heat exchanger to be cooled. A proportion of the neutralised surfactant is removed from the loop, whilst the remainder is fed back to the point of injection of the acid and the alkali, and passes around the loop again.

The anionic surfactant or surfactant paste premix is mixed with a high active solution of alkali metal silicate comprising at least 60% by weight, preferably at least 70% by weight, of said high active solution of alkali metal silicate. This mixing may be achieved in any convenient piece of mixing equipment, and may be carried out using any order of addition of the separate or pre-mixed components.

The solid salt may be any of the salts described hereinbefore. The solid salt preferably has a particle size of from 10µm to 300µm, more preferably from 20µm to 100µm.

An additional processing step can be introduced to improve the drying of the particles. This additional step involves the addition of particulate salt, of average particle size 10-300µm, preferably 20µm to 100µm to the binder prior to the agglomeration step. The particulate salt can be, for example, alkali metal silicate, carbonate or sulphate and any mixtures thereof, and is preferably added at a level of from 1% to 20%, preferably from 5% to 15% by weight of the binder.

Any apparatus, plants or units suitable for the processing of surfactants can be used for carrying out the process in accord with the invention. For mixing/ agglomeration any of a number of mixers/agglomerators can be used. Especially preferred are mixers of the Fukae^R FS-G series manufactured by Fukae Powtech Kogyo Co., Japan; this apparatus is essentially in the form of a bowl-shaped vessel accessible via a top port, provided near its base with a stirrer having a substantially vertical axis, and a cutter positioned on a side wall. The stirrer and cutter may be operated independently of one another and at separately variable speeds. The vessel can be fitted with a cooling jacket or, if necessary, a cryogenic unit.

Other similar mixers found to be suitable for use in the process of the invention include Diosna^R V series ex Dierks & Söhne, Germany; and the Pharma Matrix^R ex T K Fielder Ltd., England. Other mixers believed to be suitable for use in the process of the invention are the Fuji^R VG-Cseries ex Fuji Sangyo Co., Japan; and the Roto^R ex Zanchetta & Co srl, Italy.

Other preferred suitable equipment can include Eirich^R, series RV, manufactured by Gustav Eirich Hardheim, Germany; Lödige^R, series FM for batch mixing, series Baud KM and series CB for continuous mixing/agglomeration, manufactured by Lödige Maschinenbau GmbH, Paderborn Germany; Drais^R T160 series, manufactured by Drais Werke GmbH, Mannheim Germany; and Winkworth^R RT 25 series, manufactured by Winkworth Machinery Ltd., Berkshire, England.

The Littleford Mixer, Model #FM-130-D-12, with internal chopping blades and the Cuisinart Food Processor, Model #DCX-Plus, with 7.75 inch (19.7 cm) blades are two examples of suitable mixers. Any other mixer with fine dispersion mixing and granulation capability and having a residence time in the order of 0.1 to 10 minutes can be used. The "turbine-type" impeller mixer, having several blades on an axis of rotation, is preferred. The invention can be practiced as a batch or a continuous process.

The introduction of the fluid binder into the mixer can be done in many ways, from simply pouring to high pressure pumping through small holes at the end of the pipe, before the entrance to the mixer. The use of high pumping pressures prior to the entrance in the mixer results in an increased activity in the final agglomerates. By combining both effects, and introducing the fluid binder through holes (extrusion) small enough to allow the desired flow rate but that keep the pumping pressure to a maximum feasible in the system, highly advantageous results are achieved.

It is also within the scope of the present invention that the resulting detergent particles are dusted with a suitable solid surface coating agent such as a dusting agent, to improve particle flow properties. The dusting agent is preferably added at a level of from 0.5% to 8%, preferably from 2% to 5% by weight of the particle. Preferred dusting agents include Zeolite A and micronised calcium carbonate.

Detergent Compositions

The surfactant agglomerate particles of the invention may also be incorporated into detergent compositions for use in essentially any laundering, washing or cleaning processes, including laundry and automatic dishwashing detergent compositions.

The compositions may in addition comprise in general terms those ingredients commonly found in detergent products which may include additional surfactants, builders, bleaches, bleach activators, dispersants, suds suppressors, chelants brighteners, enzymes and soil release agents.

These ingredients may be incorporated into the product as distinct particulate components, agglomerated particulate components or as spray-on components in which the liquid ingredient is sprayed on to some, or all of the particulate components of a granular product. Additional surfactant components may include additional anionic surfactants, nonionic surfactants such as ethoxylated alcohols or polyhydroxy fatty acid amide surfactants. Builder components may include citrate, zeolite and crystalline layered silicate builders. Bleach components may include perborate and percarbonate bleaches, organic peroxyacids and bleach activators. Suitable suds suppressors may include silicone suds suppressors. Suitable enzymes may include amylolytic, proteolytic and lipolytic enzymes. More complete descriptions of typical detergent ingredients are given in European Patent Applications Nos 92914366.7 and 93913595.2 in the name of the Procter & Gamble Company.

Examples

1. Particulate agglomerate particles A and B, in accordance with the invention, were prepared with the following compositions by weight.

Binder	A	B
Sodium silicate ($\text{Na}_2\text{O} : \text{SiO}_2$ ratio = 2:0)	8.8	10.4
Sodium, $\text{C}_{12}\text{-C}_{15}$ alkyl ethoxysulfate with average degree of ethoxylation of 3.	10.0	11.6
Sodium carbonate	3.7	-
Water	10.0	10.0
Base Powder		
Sodium silicate ($\text{Na}_2\text{O} : \text{SiO}_2$ ratio = 2:0)	23.6	23.6
Sodium sulfate	35.5	35.5
Sodium carbonate	5.5	5.5
Dusting agent		
Sodium aluminosilicate zeolite (zeolite A)	2.9	2.9

The particles A were made by the following process, in accord with the invention: The sodium silicate, as a 75% active solution, and alkyl ethoxysulfate, as a 70% active paste were mixed in a liquids mixer. Finely ground sodium carbonate was added to the fluid mix to give a mixed fluid/powder binder. The silicate and sulfate components of the base powder were premixed in a powder premixer, and then mixed with the binder in a CB Loedige mixer. The resulting mix was then transferred to a KM Loedige agglomerator. The sodium carbonate was added during the agglomeration step to aid drying of the particles. Drying was then carried out in a fluid bed drier. The dry particles were then dusted with the zeolite dusting agent in a CB Loedige apparatus. The resulting particles were free flowing with acceptable hardness and solubility characteristics.

The particles B were made in an identical process to that described above for making particles B, except that no finely ground sodium carbonate was added to the fluid binder.

Claims

1. A particulate agglomerate detergent component comprising a solid salt, and a binder, wherein said binder is applied as a fluid and comprises
 - a) at least 20% by weight of alkali metal silicate; and
 - b) at least 30% by weight of anionic surfactant
 such that the weight ratio of said anionic surfactant to said alkali metal silicate is from 1:3 to 3:1.
2. A particulate agglomerate detergent component according to Claim 1 wherein said binder additionally incorporates from 1% to 20% by weight of particulate salt selected from the group consisting of alkali metal silicate, carbonate and sulphate salts, and any mixtures thereof, wherein the average particle size of the particulate salt is from $10\mu\text{m}$ to $300\mu\text{m}$.
3. A particulate agglomerate detergent component according to either of Claims 1 or 2 wherein said anionic surfactant is alkyl ethoxysulfate surfactant.
4. A particulate agglomerate detergent component according to any of Claims 1 - 3 wherein said salt comprises a mixture of sodium silicate of $\text{SiO}_2 : \text{Na}_2\text{O}$ ratio of from 2.2:1.0 to 1.8:1.0 and sodium sulfate at a weight ratio of sodium silicate to sodium sulfate of from 2:1 to 1:1.
5. A process for making a particulate agglomerate detergent component comprising the steps of:
 - a) mixing an anionic surfactant with a high active solution of alkali metal silicate comprising at least 60% by weight, preferably at least 70% by weight of the alkali metal silicate, to form the fluid binder.
 - b) agglomerating a solid salt with an effective amount of the binder to form discrete particles
 - c) drying of the agglomerated particles
6. A process for making a particulate agglomerate detergent component according to Claim 5 wherein said binder comprises
 - a) at least 20% by weight of said alkali metal silicate; and
 - b) at least 30% by weight of said anionic surfactant such that the weight ratio of the anionic surfactant to the alkali metal silicate is from 1:3 to 3:1

7. A process for making a particulate agglomerate detergent component according to either of Claims 5 or 6 comprising the additional step of adding particulate salt selected from the group consisting of alkali metal silicate, carbonate and sulphate salts, and any mixtures thereof, of average particle size from 10 to 300 μ m to the binder prior to agglomerating the solid salt with said binder.

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8. A process according to claim 7 wherein said finely ground powder is added at a level of from 1% to 20% by weight of said binder.

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9. A process according to any of Claims 5-8 wherein said anionic surfactant is alkyl ethoxysulfate surfactant.

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European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 93 30 8801

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
Y	US-A-4 169 806 (J.E.DAVIS ET AL.) * column 1, line 11 - line 21 * ---	1	C11D3/08 C11D11/00
Y	GB-A-2 209 172 (UNILEVER PLC) * page 3, paragraph 3 * * page 4, paragraph 2 -paragraph 3 * * claim 11 * ---	1	
Y	US-A-3 888 781 (G.W.KINGRY ET AL.) * column 2, line 15 - line 35 * ---	1	
A	US-A-3 887 614 (RINNOSUKE SUSUKI ET AL.) * claims 1,4,6 * ---	1	
A	FR-A-2 135 285 (MILES LABORATOIRES INC.) * claims 1-6 * -----	1	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			C11D
The present search report has been drawn up for all claims			
Place of search		Date of completion of the search	Examiner
BERLIN		10 March 1994	Pelli Wablat, B
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- & : member of the same patent family, corresponding document	